



## History of bonding and adhesives | adhesives and sealants

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FEICA, the Association of the European Adhesive & Sealant Industry is a multinational association representing the European adhesive and sealant industry. With the support of its national associations and several direct and affiliated members, FEICA coordinates, represents and advocates the common interests of our industry throughout Europe. In this regard FEICA aims to establish a constructive dialogue with legislators in order to act as a reliable partner to resolve issues affecting the European adhesive and sealant industry.

### Introduction

Man first exploited bonding technology 200,000 years ago. Today, innovation continues apace. The history of bonding is a fascinating tribute to human ingenuity.

An adhesive can be defined as a substance that causes two surfaces to stick together. By this definition, the earliest “adhesive” could be considered to have been developed three billion years when primordial cells produced a tacky outer membrane allowing them to stick to adjacent cells. The first use of adhesives by humans can be dated to around 80,000 B.C. This paper provides a convenient timeline for the history of bonding and adhesives.

### Over the years

#### 3 billion years ago

Bonding-type processes in primordial cells: They produce a tacky outer membrane which allows them to stick to each other to form colonies. There are many other examples of natural adhesives: Mussels form high-strength bonds to a wide variety of surfaces; Sundew plants and spiders produce tacky secretions; Bees produce plates of wax; Birds make the first “bonded” composite materials for nest building.

#### 200,000 years ago

Birch-bark-tar used to glue stone arrow heads to a shaft.

#### 80,000 years ago

In excavations, bonding materials have been identified as decoration on skulls, as sealants for containers and as an adhesive.

### **3,500 years ago**

Animal blood and protein are used as a binder for the base surface for cave paintings; Huts are constructed of wood and reeds strengthened with adhesive.

### **8,000 B.C.**

Resins from trees are used to assist in fixing flint and bone arrow and spear heads to wooden handles/shafts; "Adhesive pastes" are produced by boiling down plant components; "Glues" are produced by boiling down animal components.

### **5,000 B.C.**

In Mesopotamia and Egypt, naturally occurring asphalt is used as an adhesive in for example mosaics and, in combination with resins, as a sealant for boats. Animal blood, protein, various plant resins and asphalt were used as adhesives to build houses and temples

### **4,000 years ago**

Foodstuffs are buried with the deceased in broken pottery vessels that had been repaired with sticky resins from tree sap. Archaeologists have also uncovered statues from Babylonian temples that have ivory eyeballs glued into eye sockets. This tar-like glue has held for almost 6,000 years.

### **3,500 B.C.**

In Egypt the occupation of adhesive-maker (Kellopsos) was born. The art of boiling glue, which the ancient Egyptians had developed, was later taken up by the Greeks and Romans.

### **2,000 B.C.**

In the Near East gelatin glue is used for furniture manufacture.

### **1,500 B.C.**

Paintings and murals show details of wood gluing operations. A casket removed from the tomb of King Tutankhamun shows the use of glue in its construction.

### **1,000 B.C.**

In China, adhesives derived from animal skins are used for lacquering work. In addition, sap from the lacquer tree is used, which evaporates and can bond up to 30 different layers.

### **200 B.C.**

The first references in literature appear detailing simple procedures for making and using animal glue.

### **1 - 500 A.D.**

The Romans and Greeks developed the art of veneering and marquetry (the bonding of thin sections or layers of wood). During this process, the making of animal and fish glues was refined and other types of adhesives were developed, such as an adhesive from egg whites to bond golf leaf. The Romans were one of the first to use tar and beeswax to caulk the planking in boats and ships.

### **1,000 A.D.**

Genghis Khan may have owed some of his military might to the power and range of his weaponry, in particular, bows made from laminated lemonwood and bullhorn bonded with an adhesive whose formula has long since been lost.

### **1300 A.D.**

The Aztecs used the adhesive properties of blood for construction work. It is the albumin in blood which gives it these bonding properties. The Aztecs mixed this animal blood into cement.

### **1500 A.D.**

The Spaniards brought rubber to Europe from Central America where it had already long been used by Aztecs and Mayans; Casein, a protein derived from milk, was the first "plastic" to be used for coating paper and bookbinding.

Adhesives were used in the building of furniture. Some of the greatest furniture and cabinet makers of all time used adhesives in their products names you will still recognise today, such as Chippendale and Duncan Phyfe.

The secret of violins made by Antonio Stradivarius was the adhesive process used to laminate his specially treated woods. His methods have also been lost in antiquity and have not been rediscovered, even with today's sophisticated analytical methods.

### **1700**

Large-scale production of glues by boiling commences, with the first commercial glue factory being established in The Netherlands to manufacture animal glue.

### **1750**

The first glue patent was issued in Britain for a fish glue. Patents were then rapidly issued for adhesives using natural rubber, animal bones, starch, and casein.

### **1830**

Natural rubber was first used as a raw material for adhesives.

### **1841**

Rubber vulcanization was discovered (Goodyear), marking the birth of synthetic plastics. It was the first time that a natural chemical was altered to make a semi-synthetic material (plastic) with new mechanical and technological properties.

### **1905**

Baekeland brings the first phenolic resin onto the market under the name "Bakelite".

### **1920**

Hermann Staudinger demonstrates the existence of macromolecules, which he characterised as polymers and which paved the way for the birth of polymer chemistry and new adhesive developments. For this work he received the 1953 Nobel Prize in Chemistry.

## 1922

BASF awarded a patent to manufacture urea-formaldehyde resins that were soluble in organic solvents.

## 1928

First production of polyvinyl chloride (PVC) in the USA; Production of polymethyl methacrylate (PMMA) as "Plexiglas" by Rohm & Haas.

## 1930

First industrial manufacture of polyvinyl acetate (PVAC), polystyrene (PS) and polyacrylonitrile (PAN).

## 1931

First stable plastic dispersion based on acrylic acid esters (BASF, Rohm & Haas) and vinyl acetate (Wacker, Hoechst); Start of production of polychloroprene.

## 1936

P. Castan (de Tre Frères, Switzerland) uses poly-addition to make plastics and invents epoxy resins, which he patents in 1939. C. Ellis (Ellis-Foster Comp. USA) discovers the rapid curing of unsaturated esters and styrene by peroxides

## 1937

The polyaddition of diisocyanates and polyols to form polyurethanes (PUR) is based on the research work of O. Bayer in Leverkusen.

## 1940

IG Farben is awarded a patent for methacrylate adhesives (today "Agomet" of Degussa, Hanau).

## 1941

Large-scale production of saturated and unsaturated polyester resins.

## 1943

Manufacture of heat-resistant silicone rubbers; In the USA, the first use of phenolic resin – polyvinyl acetates in formulations for metal-wood bonds in aircraft manufacture.

## 1946

Industrial manufacture of epoxy resins.

## 1953

V. Kriebel (USA) introduces anaerobically curing adhesives based on dimethacrylate under the name "Loctite".

## 1958

The first cyanoacrylate adhesives are introduced: "Eastman 910" in the USA and in 1960 "Sicomet" in Germany.

## 1967

First heat-resistant polyimide adhesives (up to 300°C) introduced in the USA.

## 1968

Start of development work on moisture curing polyurethane adhesives "Sikaflex" and "Betaseal" for sealing/bonding the front and rear windscreens on vehicles.

## 1970

Rapid further development of polyurethane chemistry with a wide range of 1-C (one component) and 2-C (two-component) adhesive formulations; First UV-curing acrylate formulations; development of MS-polymers in Japan, application in earthquake-proof buildings.

## 1980

Reactive hotmelt adhesives are developed.

## 1984

Development of anisotropic, conducting adhesives. The conductivity arises from direct contact of the substrates via individual filler particles (e.g. gold-coated polystyrene spheres / diameter 5 µm) in the adhesive matrix which do not touch and which are electrically conducting.

## 1988

Development of high-strength adhesives for bonding oiled steel sheets under industrial production conditions (e.g. the car manufacturing industry). This involved special hot curing 1-C epoxy resin adhesives.

## From 1990

Development of various adhesives involving a combination of curing mechanisms, e.g. cyanoacrylates which are initially cured by UV-light and then fully cured via the effect of moisture.

## 1993

Development of aerobically curing adhesives, whose curing is triggered by oxygen. Hydroperoxide formers (e.g. hydrazone) are added to these adhesives. Under oxidising conditions peroxides are produced and start the polymerization.

## 1995

Development of silane-crosslinking polyurethane prepolymers (S-PUR) that complement the range of 1-C moisture curing rubber-elastic adhesives. They have an improved balance between reactivity and storage stability, there is no bubble formation and no longer function via an isocyanate-based reaction mechanism.

2000

Development of detachable adhesive systems for repair and recycling based on a change in temperature, stress, voltage and/or pH.

## References

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